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THE CHEMICAL EVOLUTION OF THE OCEAN[1]

ALFRED C. LANE

The paper was suggested by the chemical character of the deeper mineral waters of Keweenaw Point. The fundamental ideas were stated years ago, by T. Sterry Hunt, who called attention to the fact that in the Canadian Paleozoics there is less sodium in proportion to the chlorine than in the present ocean. The same fact is true of the deeper waters, both in upper and lower Michigan. Not only so, but taking the lowest sodium chlorine ratio, which generally comes from the deepest, or one of the deepest, wells found in any water of a given geological horizon, it appears that the older this formation, the lower the ratio. The ratio of sodium to chlorine varies from 0.468 at Big Rapids, to 0.084 near the bottom of the Tamarack Mine.

TABLE I

SODIUM: CHLORINE RATIO IN MICHIGAN DEEP WATERS

Location of Water	Geological Horizon	Reference	$Na:Cl = R$	$\frac{1-1.81R}{1-0.531R}$	$\frac{1-1.81R}{0.648}$
Portsmouth	Base of Pennsylvanian	W.S. 31, No. 251	0.586	.....	.....
Big Rapids	Marshal, mio-Miss.	W.S. 31. No. 278	0.468	0.200	0.234
Midland	Marshal, mio-Miss.	W.S. 31, No. 281	0.284	0.570	0.750
Bay City	Berea, base of Miss.	An. 1901, p. 225	0.350	0.450	0.564
Alma	Traverse, mio-Devonian	W.S. 31, No. 329	0.306	0.490	0.632
Assyria	Dundee, mio-Devonian	An. 1903, p. 108	0.321	0.525	0.673
Mount Clemens	Salina, neo-Ontarian	W.S.31, No. 319	0.304	0.480	0.625
Manistee	Niagara, mio-Ontarian	W.S.31, No. 323	0.236	0.650	0.883
Britton	Niagara, mio-Ontarian	New Kedzie	0.358	0.440	0.544
Whitby, Canada	Trenton, Ordovician	18 An. U.S.G.S. p. 652	0.25	0.630	0.865
Osceola, Wis.	Potsdam, neo-Cambrian	W.S. 114, p. 240	0.214	0.700	.....
Freda, Mich.	Upper Keweenawan	An. 1903, p. 165	0.189	0.720	1.01
Tamarack Mine	Lower Keweenawan	New Wilson	0.084	0.890	1.31
Vulcan Mine	Huronian	Am. 1903, p. 155	0.000	1.000	1.515

The last two columns give the age in fractions of a hundred million years, supposing that none or all of the sodium chloride in the rivers is cyclical.

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[1] Abstract of paper read at the Ottawa meeting of the Geological Society of America, December, 1905.

One of the explanatory factors must certainly be that suggested by T. Sterry Hunt, that in river water there is always more sodium in proportion to the chlorine than in the ocean, and that hence the carbonate of sodium, as it may be supposed to be combined, is always reacting with the calcium-magnesium chloride of the ocean water, throwing out calcium carbonate, probably by organic agencies, and leaving sodium chloride in excess instead. Professor Joly, of Dublin, has based an estimate of the age of the earth upon this accumulation of sodium in the ocean, which has been criticised, because of some minor assumptions which do not affect the reason-

TABLE II

ANALYSES OF RIVER WATER

	1. Mississippi River[1]	2. Lake Superior[2]	3. Murray's Average[3]	4. Thousand Tons per in Mile
Si	0.00350	0.00317	0.008370	34.90
Al	0.00009	0.00048	0.001820	7.60
Mn.	0.00012	Sr 0.00134	0.001960	4.00
Fe	0.00008	0.00069	0.002180	9.10
Mg	0.00680	0.00278	0.007850	32.80
Ca	0.02950	0.01280	0.034100	142.17
K	0.00230	bare trace	0.002180	9.13
Na	0.01000	0.00318	0.005790	24.10
Cl	0.01610	0.00243	0.003100	12.91
(SO_4) S	0.00960	0.00124	0.004540	18.94
(PO_4) P	0.00013	B tr	0.000140	0.58
(CO_3) C	....	22.2300	....	.....
(HCO_3) C	.02160	....	0.013230	55.28
N (free am.)	0.00016	....	0.000065	basic N. 0.27
N (alb. am.)	0.000014	....	....	basic H. 0.08
Nitrites	....	....	....	......
Nitrates	0.00023	0.00077	0.00106	(AcidN.) 443
Total solids filtered	0.16750	0.05896	0.10000	762.587
Unfiltered	1.06900			
Loss in ignition				
Organic matter				
Filtered	0.02750			79
Unfiltered	0.07160			

1. C. H. Stone, Analysis of Mississippi River Water, *Science*, 1905, p. 472, with oxygen consumed: filtered, 0.0142; unfiltered, 0.0033; hardness, 10.92; turbidity, heavy (twice averaged); sediment, large; odor, none.

2. Analysis of Lake Superior water, *Annual Report*, Geological Survey of Michigan, 1903, p. 113.

3. Average river water computed from Murray in grams per kilogram or liter.

4. Average river water according to Murray, compiled from figures given by Joly and Chamberlin's *Geology*, in thousands of tons per cubic mile. Multiply by 6.524 to get total yielded in millions of tons per annum.

TABLE III

COMPOSITION OF OCEAN[1]

	1	2	3	4
Na	306.37	1.1400	1.41.80	1.570
Cl	552.17	2.0700	2.55.57	2.850
Ca	11.96	0.0500	0.05.53	0.070
Mg	37.69	0.1400	0.17.43	0.190
C	0.41	0.0020	0.00.19	0.003
S	25.62	0.0900	0.11.87	0.125
K	11.07	0.0400	0.05.02	0.060
Br	1.88	0.0078	0.00.87	0.010
O	52.83	85.7900	....	118.400
H	......	10.6700	....	14.700
	100.00	100.0000	....	

1. Composition of sea salt—Diltman in Van Hise, p. 942.
2. Composition of ocean—Clarke in Van Hise, p. 944.
3. Bulk of salts in ocean divided by antilog 16 according to Van Hise, p. 944. I do not understand how he gets these figures; they seem to be 1.24 (× antilog 14) greater than column 2, whereas, according to Van Hise's figures, the multiplier should be 1.32×antilog 14.
4. Column 2 multiplied by 1.375 giving weight of salt in units of antilog 16 tons, if the volume of the ocean is 3,200,000 cubic miles.

ing or results materially. If there has been such an accumulation, there must have been such a change in the chemical character of the water as there really appears to be upon careful study of the analyses of deep waters.

If the amount of sodium now in the ocean be N, and of chlorine C, and there is brought in each year by the rivers n, of sodium, and c of chlorine, and if we subtract from n a quantity d to obtain the net increase of sodium after allowing for that blown inland by the breezes or buried in the sediments laid down, etc., and let rd be a similar correction to be applied to the chlorine, then the ratio of sodium to chlorine (let the ratio be R) in the ocean x years ago would be, accepting a uniform rate of accumulation,

$$R=\frac{(N-x(n-d))}{(C-x(c-Rd))}$$

and

$$x=\frac{N-CR}{n-cr-d(1-rR)}$$

[1] After Van Hise, p. 193.

Substituting in this formula the numerical data used by Joly, one will get Joly's results as to the age of the earth. By assuming appropriate values of *R* one can assign a date to the burial of any brine.

N and *C* are reasonably well known. Sir John Murray's estimates, the only ones made as yet, for *c* and especially *n* are liable to be seriously in error. The quantity $d\ (1\text{-}rR)$ is likely to be a small correction, except in the case of volcanic emanations of chlorine, for in the case of most other allowance *r* is likely to be pretty nearly reciprocal to *R*.

Inserting Joly's numerical values we obtain

$$x=\frac{1.41-2.54R}{1.57-.84R-\mathrm{d}\,(1-rR)}$$

in hundreds of millions of years.

A formula involving a slightly different volume of the ocean may be as exact and is more convenient, for computation, and was used by the author.

A somewhat elaborate discussion of analyses and the probabilities of the case led to the conclusion that, while a similar formula, which was given, could be constructed for any two substances brought into the ocean by the rivers, among those abundant enough to be well determined by analysis the chlorine and sodium were the only ones likely to accumulate, and not be modified seriously in relative proportions even when buried.

Among the difficulties discussed were the high concentrations of the deeply buried waters, and the very low amount of sodium in the Keweenawan, which is by no means the base of the geological column.

The suggestion was made that perhaps the volcanic contribution to the ocean was by no means an unimportant one, and that there had been a continuous emanation of chlorinated water, adding to the volume of the ocean from the very earliest times.

The analyses upon which the paper was based have mainly been published in *Water-Supply Paper* No. 31 of the United States Geological Survey, and in the annual report of the Geological Survey of Michigan for 1903. Tables of analyses, in ionic form, were given for Murray's average river water, Lake Superior, and the Mississippi River; also of the ocean and Keweenawan mine-waters.

A diagram was also shown in which, alongside Dana's geological column (which is proportioned according to his estimates of the lengths of the geological periods), the sodium: chlorine ratio, and computed ages of various brines, were laid off horizontally, which diagram was constructed from Table I.

TABLE IV

(KEWEENAWAN WATER ANALYSES (grams per kilo)

	1	2	3	4
Sp Gr	......	......	1.0511	....
Insoluble silica	0.0222	......	....	....
Insoluble Fe_2O_3	0.0127	......	....	....
Dissolved SiO_2	0.0033	0.00005	....	....
$FeCl_2$	0.0045	......	Mn. 0.5700	....
$ZnCl_2$	0.0290	......	....	....
$CuCl_2$	0.0043	......	....	....
$MgCl_2$	0.0875	NH_4Cl 2.457	Mg_2Br 0.2400	....
NaCl	1.8800	21.009	19.2900	....
KCl	0.0740	1.595	0.5600	....
$CaCl_2$	3.1380	130.508	44.5100	....
$CaSO_4$	0.0555	0.320	......	......
$CaCO_3$	0.2480	......	....	......
Loss on ignition	1.0800	......	....	......
Sum			6.517	
Total solids on evaporation		154.4115		
Dissolved ions—				
NH_4	......	0.830	.....	....
Fe	0.0020	......	Mn 0.57	....
Zn	0.0134+Ni	Ba, Sr 0	.....	....
Cu	0.0022	......	.....	....
Mg	0.0232	tr	0.03	0.0130
Na	0.7400	8.278	7.60	2.7310
K	0.0388	0.837	0.30	
Ca	1.2496	47.166	16.04	6.3000
Cl	3.265	97.963	40.42	15.2287
SO_4	0.0392	0.226	Br 0.21	0.0724
CO_3	0.1490	0		

1. Is the water from the boiler of the vertical shaft of the Calumet and Hecla Mine, about 5,000 feet deep, but containing more or less surface water, by Heath. See *Annual Report*, 1903, p. 166.

2. Tamarack cross-cut, 4,300 feet deep—A. C. Lane, sampler; F. B. Wilson, analyst.

3. Freda Well, *Annual Report*, 1903, p. 166.

4. Wolverine Mine—seventeenth level—A. C. Lane, sampler; F. B. Wilson, analyst.